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**(54) Process for preparing 1,4-cyclohexanedicarboxylic acid**

Verfahren zur Herstellung von 1,4-Cyclohexandicarbonsäure

Procédé pour la préparation de l'acide 1,4-cyclohexanedicarboxylique

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## Description

The present invention relates to a process for preparing 1,4-cyclohexanedicarboxylic acid (hereinafter may be referred to as 1,4-CHDA).

### Background of the Invention

1,4-CHDA is useful as raw material for medical drug, synthetic resin, synthetic fiber, paint, etc. and to be more specific, is used as raw material for producing resins and fibers having excellent heat resistance, weather resistance and physical strength, etc.

Among methods for preparing 1,4-CHDA, the representative process consists in obtaining through hydrogenation of benzene ring by using a high purity terephthalic acid (hereinafter may be referred to as TPA) among those produced as industrial raw material, and a plurality of processes have already been disclosed.

These processes may be generally classified into those reducing benzene ring after having once obtained metal salts as sodium and the like or various ester from the acid part of TPA and those reducing directly from the acid.

As the former needs supplementary steps for leaving the raw material TPA as derivative, reducing before rendering it to the form of acid, the direct reduction process is more economic and have been believed to be more promising.

Among a number of trials, few have succeeded in reducing acid as it is, including for instance the process disclosed in (1) Japanese TOKKYO-KOKOKU-KOHO (Publication for Opposition of Examined Patent Application) SHOWA 36(1961)-522 wherein TPA with aqueous medium is hydrogenated under the condition of 150 to 300°C and about 210kg/cm<sup>2</sup> in a stainless pressure vessel using palladium or ruthenium as catalyst, the reaction product is dissolved in alkali such as sodium hydroxide, catalyst is filtered before adding acid for neutralization and acid dipping to obtain 1,4-CHDA of interest.

On the other hand, the process disclosed in (2) Journal of Organic Chemistry, 31(10) pp.3438-9 (1966) comprises the steps of hydrogenating TPA in aqueous medium with rhodium on alumina as catalyst under 60 to 70 °C and with the hydrogen pressure of less than 3 times the atmospheric pressure, removing catalyst by high temperature filtering and extracting 1,4-CHDA of interest with chloroform by a yield of approximately 90%.

Moreover, another process is disclosed in (3) Japanese TOKKYO-KOKAI-KOHO (18-month Publication of Unexamined Patent Application) SHOWA 58(1983)-198439 wherein TPA with aqueous medium is hydrogenated under the condition of 150 °C and about 100kg/cm<sup>2</sup> in a stainless steel pressure vessel using palladium or ruthenium as catalyst, which are then separated under a specific temperature condition within the range of 110 to 180 °C and defined as  $t \geq 43.5 \times \log_{10} C + 69.5$  ( $t$  = degree Celsius,  $C$  = 1,4-CHDA dissolved amount to 100 weight parts of water expressed by weight part) to obtain 1,4-CHDA of interest.

Recently, as the demand for product having an international competitive power and high level functions in the field of medical drugs or the field of resins where 1,4-CHDA is used as raw material, it is required that raw material of extremely low impurity though offering an international cost competitive power such as high purity product of which 1,4-CHDA purity is approximately 99.9 weight %, those containing little mineral like chlorine or those containing less impurities such as affinities of cyclohexanecarboxylic acid be supplied without a significant rise in price.

1,4-CHDA obtained by the conventional processes, however, was not pure enough to satisfy such a high level quality demand and even if some special preparation method could be considered, it would remain impractical because it will need extremely complicated and expensive process.

For instance, when followed up, the process (1) above presents difficulties such as a dramatic loss of catalyst activity which is necessary for the reduction and, in consequence, an extremely high catalyst cost.

Additionally, a fateful problem remained unresolved, namely, it has been impossible to prevent impurities from being mixed in 1,4-CHDA, impurities such as 4-methylcyclohexanecarboxylic acid and other affinities of cyclohexanecarboxylic acid, byproducts of the reaction, sodium sulfate, sodium chloride and other minerals produced by the acid for recovering 1,4-CHDA from alkali used for dissolving raw material TPA or from reaction products of the hydrogenation.

In consequence, irregular reactions may be caused by the impurities contained in the raw material during the polymerization of resin or others using as raw material 1,4-CHDA obtained by this process or the heat resistance, the physical strength or the weather resistance of the final product such as resin may be significantly deteriorated by the impurities contained in the raw material and the other disadvantages have been remarked and the improvement of these disadvantages remains unresolved.

In the process (2) above, like the abovementioned (1), though the price is ten times higher than palladium or ruthenium, the catalyst life of rhodium used as catalyst is not longer in proportion to the price, the purity of the product of interest in the reaction product is so low as approximately 95% and, moreover, it has been impossible to prevent impurities such as affinities of cyclohexanecarboxylic acid, reaction byproducts, from being mixed in 1,4-CHDA.

Additionally, chloroform used as extraction medium in the preparation according to this process dissolves well the above-mentioned impurities equally so, in consequence, the resulting purity of 1,4-CHDA is not significantly different

from the purity before the extraction. Moreover, as this medium itself is a poison, its use itself is not preferable and the use of medium other than water requires additional cost for equipment and for extraction of the medium. The improvement of these difficulties has also been left unresolved.

While in the process (3) above, though exempt from sodium sulfate, sodium chloride and other minerals produced from alkalis and acids, affinities of cyclohexanecarboxylic acid are produced as byproduct of the hydrogenation in which palladium or ruthenium is used as catalyst at 110 to 180 °C and it has been impossible to prevent these impurities being mixed in 1,4-CHDA.

As a means to resolve these problems, it would be possible to crystallize the product containing 1,4-CHDA; however, as 1,4-CHDA and impurities are extremely insoluble to the water, it is impossible to obtain a high purity product showing the purity of at least 99.9% by crystallizing 1,4-CHDA of which purity is less than 99.5% when the crystallization is undertaken from the water.

On the other hand, a high temperature and/or a high pressure are required so as not to leave some raw material non reduced in function of the repeated use of the catalyst, but 1,4-CHDA purity of the reaction product decreases because of such a severe temperature condition. This disadvantage has not also been resolved.

In the preparation processes of 1,4-CHDA described above, the example of preparation using new catalyst which is not deprived of the activity is disclosed and it seems apparently that they would permit to obtain 1,4-CHDA of relatively high purity. The inventors have, however, followed up these processes and found that 1,4-CHDA of low purity is produced almost in any of them and the product could not be used as it is.

The reason seems to be as follows : in many cases, impurities are produced but absorbed preferentially by the absorption points such as active carbon used as catalyst carrier, in consequence, though the apparent 1,4-CHDA purity is relatively high, as the absorption capacity of active carbon and other is limited, the impurities could be detected at the rate as they are produced in reality once the absorption capacity has been attained.

On the other hand, a stainless steel pressure vessel is adopted for the conventional preparation methods, but the inventors have made a detailed research on a conventional stainless vessel by introducing solution of TPA or 1,4-CHDA therein and making contact with the vessel wall at a temperature at which the hydrogenation will take place and found that nickel, iron, chrome, molybdenum and other components of the stainless steel are dissolved in the solution and, acting as catalytic poison, lower significantly the catalyst activity.

Given these restrictions, the conventional processes can not allow an economical production due to rapid decrease of catalyst activity, the reaction product can not meet recent severe requirements because the conventional reaction produces more impurities than the expectation during the preparation of 1,4-CHDA and, moreover, it is also difficult to improve the purity of 1,4-CHDA through the conventional processes, so the development of a method that could resolve various problems mentioned above has been expected eagerly.

US-A-5 159 109 discloses a method for removing impurities in 1,4-cyclohexanedicarboxylic by steam distillation in a process for crystallizing 1,4-cyclohexanedicarboxylic acid. However, 4-methyl-1-cyclohexanedicarboxylic acid (MCHCA), one of the impurities, is difficult to be separated by the steam distillation. Plenty of steam is required to obtain a high purity 1,4-cyclohexanedicarboxylic acid by this method. Particularly, plenty of steam is required when MCHCA is taken in a crystal of 1,4-cyclohexanedicarboxylic acid.

#### Disclosure of the Invention

The inventors have made a study on the behavior of TPA and its alkali salt against various reactions, examined actively the realization of its economical process and the method for improving the product purity, found that the drop of catalyst activity is provoked by nickel, chromium, molybdenum, iron and others dissolved from the wall of a metal pressure vessel made, for instance, of stainless steel which is conventionally used, succeeded in realizing an economical hydrogenation with a remarkable suppression of the drop of catalyst activity through the adoption of a vessel providing a high acid resistance or a vessel provided with a layer of highly acid resistant material as a reactor and, moreover, succeeded in obtaining extremely high purity 1,4-CHDA by bringing the solution containing hydrogenation product into contact with the steam and thus in completing the invention.

Now the content of the present invention will be described in detail.

First, the present invention is a process for preparing 1,4-cyclohexanedicarboxylic acid as defined in claim 1.

Second, the present invention is a process for preparing 1,4-cyclohexanedicarboxylic acid of the claim 1, wherein the hydrogenation of the first step is performed under a hydrogen pressure between 2kg/cm<sup>2</sup> and less than 10kg/cm<sup>2</sup>.

Third, the present invention is a process for preparing 1,4-cyclohexanedicarboxylic acid of the claim 1 or 2, wherein the hydrogenation of the first step is performed in a pressure vessel provided with a vitreous layer.

Fourth, the present invention is a process for preparing 1,4-cyclohexanedicarboxylic acid of the claim 1, 2 or 3 wherein, in the second step, 1,4-cyclohexanedicarboxylic acid is brought continuously into contact in counterflow with steam by supplying the solution containing 1,4-cyclohexanedicarboxylic acid continuously from one side of a packed tower, supplying steam continuously from the opposite direction thereof, withdrawing (evacuating) 1,4-cyclohexanedi-

carboxylic acid discontinuously or continuously from the other side while withdrawing (evacuating) steam in the opposite direction thereof and removing impurities extracted by (moved to) the steam side by condensing them with the steam or by passing the steam through an alkaline aqueous solution before reheating for steam recycling as necessary.

As for the quality of TPA used for the present invention, saying nothing of high purity products that have been used conventionally as raw material of 1,4-CHDA, those of general industrial use quality that have not been used conventionally because of their slightly lower purity can be adopted advantageously; however it is preferable that they contain little metal ions which would act as a catalyst poison during the hydrogenation reaction.

Additionally, the preferable TPA concentration for the embodiment of the present invention is 5 to 50% for the first step; however, more preferable concentration is 10 to 40%.

In the embodiment of the present invention, a concentration higher or lower than the said concentration range of the first step is not preferable in both cases, because the production will not be so effective as the equipment scale if it is lower than 5% and because the handling will be difficult due to a poor solubility of trans-isomer if it is higher than 50%.

As a catalyst for the hydrogenation reaction used advantageously in the present invention, metal palladium carried on a catalyst support can be adopted advantageously and as a catalyst support, carbon represented by various activated charcoals is most preferable among alumina, silica or carbon because it is hardly affected by acid.

The palladium supported amount adopted advantageously for the embodiment of the present invention is 2 to 20%, expressed by the rate of metal palladium content in the catalyst weight, while 5 to 10% is more preferable.

In the embodiment of the present invention, various alcohols, water or 1,4-CHDA can be used as a medium for controlling the concentration; however, the water is most preferable because it is inert to the reaction and the price is low.

Concerning highly acid resistant material and highly acid resistant vessel, highly acid resistant metals such as hastelloy steel, inconel steel and their compact or non metallic highly acid resistant materials such as ceramics, enamel, glass or other vitreous material or their compact or vessels made of iron or stainless steel used for an ordinary pressure vessel and provided with a lining of various acid resistant materials mentioned hereabove are used.

The parameters for an advantageous embodiment of the first step of the present invention includes the temperature of 120 to 160 °C, the hydrogen pressure of 1 to 50kg/cm<sup>2</sup> or more preferably between 2kg/cm<sup>2</sup> and less than 10kg/cm<sup>2</sup> and the reaction time of 30 to 120 minutes and the deviation from this range is not desirable in any case because the yield and the purity of the product will be affected adversely.

As for the concentration of the reaction product containing 1,4-CHDA used for the second step, it is most economic to use the concentration of the filtrate as it is after the removal of catalyst following the hydrogenation; however, given the rate of cis- and trans-1,4-CHDA obtained usually, economic restrictions and the solubility into the water, the concentration range of approximately 2% to 40% is preferable and the range from 5% to 30% is most preferable.

Moreover, there is no specific restriction as for the proportion of cis- and trans-1,4-CHDA contained in the reaction product containing 1,4-CHDA and their proportion which would appear in the reaction product obtained by the hydrogenation of TPA does not interfere the embodiment of the present invention; however the dissolution temperature reaction product to the water generally tends to increase as increases the proportion of trans-1,4-CHDA and the proportion of cis- : trans-1,4-CHDA = approximately 80 : 20 to 50 : 50 is suitable for the operation.

There is also no particular restriction for the steam used in the second step of the present invention and those produced by an ordinary steam generator are satisfactory provided that they allow to meet the temperature requirement of the embodiment of the present invention.

In the second step, solution containing 1,4-cyclohexanedicarboxylic acid is brought into contact with steam by batch or continuously and both methods may be adopted for the present invention admitting that the continuous method is more efficient.

On the other hand, the method to remove impurities moved to the steam side after the contact of 1,4-CHDA with the steam may also be carried out both by batch or continuously and it can be performed by removing the mixture of impurities and steam drain by means of condensation of the steam, by injecting steam into the alkaline aqueous solution or by introducing steam into the shower of alkaline aqueous solution.

Moreover, as a preferable embodiment of the second step of the present invention, the said solution containing 1,4-cyclohexanedicarboxylic acid and steam may be brought into contact in counterflow.

Steam may arbitrary be recycled in order to reduce the energy loss throughout the process and, as mentioned above, after having removed impurities by means of alkaline aqueous solution, the steam may be heated as necessary for the reuse.

The abovementioned respective operation of the second step may certainly be combined arbitrary, however, among such combinations, the method comprising the steps of bringing solution containing 1,4-CHDA and steam into contact in counterflow, bringing steam containing impurities into contact with alkaline aqueous solution in order to absorb impurities by the alkaline aqueous solution before reusing the steam is most advantageous from the economic point of view.

Now the method of combination will be described more in detail. First, a tower (A) and a tower (B) filled with charge such as Raschig rings are provided, then an upper portion of the tower (A) and an lower portion of the tower (B), a lower

portion of the tower (A) and an upper portion of the tower (B) are connected respectively through piping, each of pipings and towers is provided with a structure such as jacket, etc. that would allow to adjust to the predetermined temperature and a pump (P) having a function to circulate the steam in the middle of the piping connecting the lower portion of the tower (A) and the upper portion of the tower (B) positioning the tower (A) at the evacuation side.

Next, operating the pump (P) of the said equipment, heated solution containing 1,4-CHDA is introduced continuously from the upper portion of the tower (A) and evacuated from the lower portion of the tower (A) and at the same time, heated alkaline aqueous solution is introduced continuously from the upper portion of the tower (B) and evacuated from the lower portion of the tower (B).

At this time, the preferable concentration of the solution containing 1,4-CHDA supplied to the tower (A) is 2 to 40%, but more preferable is 5 to 30%.

On the other hand, the preferable concentration of the alkaline aqueous solution supplied to the tower (B) is 1 to 50%, but more preferable is 1 to 20%.

The preferable flow rate of the solution containing 1,4-CHDA supplied to the tower (A) is about 1 to 6 times the capacity of the tower (A) per hour depending on its concentration, temperature or the content of impurities contained therein.

Here, the flow rate of 1,4-CHDA less than 1 time per hour is not preferable because it lowers the efficiency of production unnecessarily and the flow rate more than 6 times per hour is also undesirable because the removal of impurities may become imperfect.

Moreover, the preferable flow rate of the alkaline aqueous solution supplied to the tower (B) is about 1 to 6 times the capacity of the tower (B) and the flow rate superior or inferior to this range is, in both case, undesirable because alkali may become excessive or insufficient.

As for the alkali in this invention, sodium hydroxide, potassium hydroxide or sodium triphosphate may be used advantageously, but among various alkalis, salts of calcium often provoke scale and carbonates generate gas; therefore they are both recommended not to adopt though they can be used.

The preferable steam circulation rate by the pump (P) is approximately 0.1 to 1.6 times of the tower (A) capacity per hour when it is converted in the volume of steam condensed water and any deviation from this range in both sides may affect adversely the cost or yield of the second step and, therefore, is not desirable.

When the second step of the abovementioned combination is adopted, it is recommended to keep the temperature of respective tower and piping within 100 to 150 °C or more preferably within 102 to 130 °C and the difference in temperature of the tower (A) and the tower (B) is not undesirable because the supplied solution containing 1,4-CHDA may boil or the steam may condensate in a way to imbalance the mass balance on one hand and a temperature inferior to 100 °C may provoke insufficient removal of impurities and a temperature exceeding 150 °C is also undesirable because it may decrease the yield due to the decomposition, etc. on the other hand.

In the said tower (B), the velocity with which impurities contained in the steam is absorbed and move toward alkali side is so rapid, a method wherein the steam containing impurities coming from the upper portion of the tower (A) is brought into contact with a shower-form alkaline aqueous solution or a method wherein the steam is blown directly into the alkaline aqueous solution may be adopted.

As described hereinabove, the embodiment of the present invention permits to suppress the activity drop of hydrogenation catalyst and to assure a long catalyst life and this permits to realize economically a method for obtaining 1,4-CHDA by subjecting TPA directly to the hydrogenation reaction and, moreover, to prepare 1,4-CHDA of high quality that will meet with the actual severe requirement.

The embodiment of the present invention permits to realize an economical hydrogenation reaction through a significant suppression of the catalyst activity loss of expensive palladium, to obtain an extremely high purity 1,4-CHDA with very simple operations by bringing the said solution containing hydrogenation product into contact with the steam and to produce resins showing excellent weather resistance or physical strength or high purity medical drugs.

#### Brief description of the Drawings

Fig. 1 is a schematic diagram for the first Example of the equipment provided with heating jacket to be used for the embodiment of the present invention.

Fig. 2 is a schematic diagram for the second Example of the equipment provided with heating jacket to be used for the embodiment of the present invention.

References in the drawings indicated respectively :

A: Tower, B: Tower, C: Tower,

a: Inlet, b: Steam outlet, c: Steam inlet, d: Outlet, e: Alkaline liquid inlet, f: Steam outlet, g: Steam inlet, h: Alkaline liquid outlet, i: Alkaline liquid inlet, j: Steam outlet, k: Alkaline liquid outlet, m: Steam inlet,

1: Vessel, 2: Column, 3: Liquid receiving vessel, 4: Vessel, 5: Column, 6: Liquid receiving vessel, 7: Pump, 8: Pump, 9: Steam circulation pump, 10: Vessel, 11: Alkaline shower equipment, 12: Liquid receiving vessel, 13: Pump, 14: Pre-

heater, 15: Preheater

# Preferred Embodiments

5 Now the present invention will be illustrated more specifically by the followings reference examples and embodiment examples referring to the attached drawings, however, these examples are not intended to limit the scope of the present invention.

## [Embodiment example 1] (First step)

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30 g of terephthalic acid, 270 g of water and 8 g of 10% palladium-carbon catalyst (supplied by N.E. Chemcat Corporation) are introduced into a glass autoclave of 500 ml provided with agitator blades made of fluororesin (Teflon) and hydrogenated at 130 °C under a hydrogen pressure of 8.3 to 9.8 kg/cm<sup>2</sup> and the reaction stops after 50 minutes when the hydrogen absorption is no more observed.

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The reaction liquid is evacuated from the autoclave, all the catalyst is filtered off for recovering, the recovered catalyst is washed with 2000 ml of boiling water before adding it to the filtrate.

The filtrate is then analyzed by gas-liquid chromatography and the 1,4-CHDA purity in the solid component is found to be 98.4 %, the non reduced material to be 0.02 % and impurities to be composed only of 4-methylcyclohexanecarboxylic acid and cyclohexanecarboxylic acid.

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Then the similar hydrogenation is repeated adding 30 g of terephthalic acid and 270 g of water to the recovered catalyst.

The hydrogenation is repeated up to 70 times using the recovered catalyst, however, a significant variation of reaction time, 1,4-CHDA purity or volume of non reduced material that are as much indices of hydrogenation activity of the catalyst is not observed.

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The results of the repeated hydrogenation are shown in the following Table 1.

Table 1

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Repeated times	Reaction time (minute)	Purity of 1,4-CHDA (%)	Non reduced material (%)
1	50	98.4	0.02
10	53	97.7	0.02
20	53	97.6	0.02
40	55	97.7	0.01
70	55	97.6	0.02

35

## 40 [Reference example 1] (First step)

The hydrogenation is repeated up to 20 times as in the Embodiment example 1 except that a stainless autoclave is used in place of glass one of the Embodiment example 1.

As the result, the time necessary for the hydrogenation is prolonged and further repetition is abandoned. The results of the repeated hydrogenation are shown in the following Table 2.

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Table 2

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Repeated times	Reaction time (minute)	Purity of 1,4-CHDA (%)	Non reduced material (%)
1	55	98.4	0.01
10	75	97.1	0.01
20	145	97.8	0.02
Abandoned thereafter			

55

[Embodiment example 2] (First step)

1.2 kg of terephthalic acid, 4.8 kg of water and 240 g of 10% palladium-carbon catalyst are introduced into a stainless (SUS306) autoclave of 10,000 ml provided with glass lining on the inner wall and liquid contact portion of agitator blades and hydrogenated at 130 °C under a hydrogen pressure of 8.5 to 9.8 kg/cm<sup>2</sup> and the reaction stops after 65 minutes from the beginning of the reaction when the hydrogen absorption is no more observed.

The reaction liquid is cooled down, evacuated from the autoclave, filtered at 135 °C by an enamel pressure filter of 10 liters, cooled down and the filtrate is then analyzed to find 1,4-CHDA purity be 97.4 % and the non reduced material be 0.02 %.

[Embodiment example 3] (First step)

600 g of terephthalic acid, 5.4 kg of water and 120 g of 10% palladium-carbon catalyst are introduced into the same autoclave as the Example 2 and hydrogenated at 140 °C under a hydrogen pressure of 5 to 6 kg/cm<sup>2</sup> and the reaction stops after 115 minutes from the beginning of the reaction when the hydrogen absorption is no more observed.

The reaction liquid is cooled down and, as in the Example 2, heat filtered, cooled down and the filtrate is then analyzed to find 1,4-CHDA purity be 96.5 % and the non reduced material be 0.03 %.

[Embodiment example 4] (First step)

The hydrogenation is carried out as in the Example 3 except that 240 g of 7.5% palladium-carbon catalyst is used, the reaction temperature is 150 °C and the hydrogen pressure is 8.5 to 9.8 kg/cm<sup>2</sup>. In consequence, the reaction time is 75 minutes from the beginning of the reaction. The analysis shows that 1,4-CHDA purity is 96.8 % and the non reduced material is 0.03 %.

[Embodiment example 5] (First step)

900 g of terephthalic acid, 5.1 kg of water and 400 g of 5% palladium-carbon catalyst are introduced into the same autoclave as the Example 2 and hydrogenated at 130 °C under a hydrogen pressure of 8.5 to 9.8 kg/cm<sup>2</sup> and the reaction stops after 65 minutes from the beginning of the reaction when the hydrogen absorption is no more observed.

The reaction liquid is analyzed as in the Example 2 to find 1,4-CHDA purity be 98.2 % and the non reduced material be 0.01 %.

[Embodiment example 6] (Second step)

A equipment provided with a heating jacket shown in Fig. 1 wherein a stainless tower (B) provided with a jacket and the other portions in contact with liquid are respectively layered with a glass lining is supplied and connected to pipings provided with heating jacket as shown in the drawing.

The dimensions of respective component of the tower (A) shall be : vessel (1) (inner diameter 5 cm, length 20 cm), column (2) (inner diameter 5 cm, length 198.7 cm, capacity 3900 ml), liquid receiving vessel (3) (inner diameter 5 cm, length 70 cm) and those of the tower (B) shall be : vessel (4) (inner diameter 5 cm, length 20 cm), column (5) (inner diameter 5 cm, length 198.7 cm, capacity 3900 ml), liquid receiving vessel (6) (inner diameter 5 cm, length 70 cm) and the column (2) is filled with ceramic Raschig rings (inner diameter 3 mm, outer diameter 6 mm, length 6 mm) and the column (5) with wire gauze of 5 mm x 12 mm respectively.

On the other hand, are attached respectively an inlet of solution containing 1,4-CHDA (a) on the top and a steam outlet (b) on the side of the vessel (1), a steam inlet (c) on the side and an outlet port (d) of 1,4-CHDA at the bottom of the liquid receiving vessel (3), an inlet of alkaline aqueous solution (e) on the top and a steam outlet (f) on the side of the vessel (4) and a steam inlet (g) on the side and a evacuation port of alkaline aqueous solution (h) at the bottom of the liquid receiving vessel (6).

First, a steam pressure of 4.8 kg/cm<sup>2</sup> is applied to the jacket portion of the equipment and the temperature in the system is adjusted to 150 °C then the steam circulation pump (9) is driven at a flow rate of 57 ml (volume as water) per minute to advance steam to the steam inlet (c) for circulating the steam in the equipment.

Then the pump (8) is driven to supply 10 % aqueous solution of sodium hydroxide to the inlet (e) through a pre-heater (15) at a flow rate of 67 ml per minute and the solution containing 1,4-CHDA obtained in the Example 2 (concentration of 20 %, 1,4-CHDA purity of 97.4 %) is supplied by the pump (7) at a flow rate of 133 ml per minute and respective liquids are evacuated from the drain port (d) and evacuation port (h) of respective tower every 10 minutes.

One (1) hour and two (2) hours after, the solution containing the produced 1,4-CHDA is extracted from the evacuation port (d) of the liquid receiving vessel (3), analyzed and no impurity is found.

[Embodiment example 7] (Second step)

The treatment is performed adopting the same method as the Example 6 except for the following parameters.

5 The temperature in the piping and the equipment is adjusted to 130 °C, the solution obtained under the conditions of the Example 5 (concentration of 15 %, 1,4-CHDA purity of 98.2 %) is used as solution containing 1,4-CHDA, the supply rate to the inlet (a) is 266 ml per minute and the supply rate of 10 % aqueous solution of sodium hydroxide to the inlet (e) is 67 ml per minute.

10 The equipment is driven with the steam circulation pump (9) running at the supply rate of 71 ml (as water volume). One (1) hour and two (2) hours after, the solution is extracted from the evacuation port (d) of the liquid receiving vessel (3), analyzed and no impurity is found.

[Embodiment example 8] (Second step)

15 The equipment is operated same as in the Example 6 except that the temperature in the equipment of the Example 6 is adjusted to 110 °C, the solution obtained under the conditions of the Example 3 (concentration of 10 %, 1,4-CHDA purity of 96.5 %) is used as solution containing 1,4-CHDA, the supply rate to the inlet (a) is 200 ml per minute, and 5 % alkali aqueous solution is used and its supply rate to the inlet (e) is 134 ml per minute and the equipment is driven as in the Example 6 with the steam circulation pump (9) running at the supply rate of 71 ml (as water volume). One (1) hour and two (2) hours after, the solution is extracted from the evacuation port (d) of the liquid receiving vessel (3), analyzed and no impurity is found.

[Embodiment example 9] (Second step)

25 As the tower (B) of the Example 6, a stainless steel vessel (inner diameter 12 cm, length 100 cm, capacity 11300 ml) without filling is adopted and a check valve is mounted between the steam outlet (b) and the steam inlet (g) for preventing the water back flow and for letting the steam flow from the steam outlet (b) to the steam inlet (g).

5000 ml of 20 % potassium hydroxide is introduced so that the steam inlet (g) of the vessel (B) will be under the level of alkali aqueous solution and the temperature of the whole system is maintained at 130 °C.

30 The solution containing 1,4-CHDA obtained under the conditions of the Example 5 (concentration of 15 %, 1,4-CHDA purity of 98.2 %) is supplied from the inlet (a) at a flow rate of 67 ml per minute and the equipment was operated as in the Example 6 except that the continuous supply and evacuation of alkali is omitted. One (1) hour and two (2) hours after, the solution is extracted from the evacuation port (d) of the liquid receiving vessel (3), analyzed and no impurity is found.

35 [Embodiment example 10] (Second step)

Using only the tower (A) of the Example 6, a piping is connected to the steam inlet (c) so that the steam of the same steam pressure as the outside jacket, a throttle valve and a cooler are attached to the steam outlet (b) so that this structure can condensate the evacuated steam.

40 A steam pressure of 2.0 kg/cm<sup>2</sup> is applied to the jacket of the equipment and piping in order to keep the temperature at 120 °C, the steam inlet (c) valve is opened to introduce steam into the equipment and the steam outlet (b) valve is opened so as to adjust the flow rate of the cooled and evacuated condensate at 57 ml per minute.

45 Then the solution containing 1,4-CHDA obtained under the conditions of the Example 4 (concentration of 10 %, 1,4-CHDA purity of 96.8 %) is supplied through the preheater (14) to the inlet (a) at a flow rate of 100 ml per minute by the pump (7) and the steam outlet (c) valve is adjusted so that the concentration of refined solution containing 1,4-CHDA evacuated from the evacuation port (d) will be 10 %.

The liquid is evacuated from the evacuation port (d) every 10 minutes, then one (1) hour and two (2) hours after, the extracted liquid is analyzed and no impurity is found.

50 [Embodiment example 11] (Second step)

55 As shown in Fig.2, a tower (C) with jacket (made of SUS316) is provided in place of the tower (B) of Example 6. As in the tower (B), the structure of the tower (C) comprises a vessel (10) (inner diameter 17 cm, length 40 cm), an alkali showering apparatus (11) (inner diameter 17 cm, length 99.6 cm, capacity 22600 ml) and a liquid receiving vessel (12) (inner diameter 17 cm, length 49.8 cm, capacity 11300 ml).

Are attached respectively an alkali liquid inlet (i) on the top and a distributor at the extremity of an alkali piping of the vessel (10) so that this structure permits the alkali liquid introduced from the alkali liquid inlet (i) to disperse uniformly in the form of shower in the alkali showering apparatus (11). Additionally, a steam outlet (j) is attached on the



side and a throttle valve and a cooler are attached on the outside of the vessel (10).

A liquid outlet port (k) is attached at the bottom and a steam inlet (m) and a valve are attached on the side of the liquid receiving vessel (12), and a pump (13) is mounted between the inlet of alkaline liquid inlet (i) and the liquid outlet port (k) so that this structure permits the liquid to circulate toward the alkali liquid inlet (i).

Moreover, the steam outlet (b) and the steam inlet (m), the steam inlet (c) and the steam outlet (j) are connected by a piping respectively and a steam circulation pump (9) is mounted between the steam inlet (c) and the steam outlet (j) so that the steam circulates toward the steam inlet (c).

First, 5000 ml of 10 % solution of sodium hydroxide is introduced in the vessel (10) of the tower (C), a steam pressure of 2 kg/cm<sup>2</sup> is applied to each jacket and the temperature is adjusted to 120 °C, then the pump (13) is driven to circulate at a speed of 6000 ml per minute and a steam circular pump (9) is driven at a flow rate of 71 ml (volume as water) per minute. At the same time, the solution containing 1,4-CHDA obtained under the parameters of the Example 5 is supplied to the inlet (a) of the tower (A) at a flow rate of 266 ml per minute and the solution containing 1,4-CHDA is evacuated from the liquid outlet port (d) every 10 minutes.

One (1) hour and two (2) hours after, the quality of the solution extracted from the evacuation port (d) is analyzed and no impurity is found.

## Claims

1. A process for preparing 1,4-cyclohexanedicarboxylic acid characterized by passing consecutively through the following two steps:

- the first step comprises the hydrogenation of a solution containing terephthalic acid in the presence of a palladium catalyst in a highly acid resistant vessel made of highly acid resistant metals such as hastelloy steel, inconel steel and their compact or non metallic highly acid resistant materials such as ceramics, enamel, glass or other vitreous material or their compact or in a vessel lined with various acid resistant materials hereabove and
- the second step comprises the contact of the solution containing 1,4-cyclohexanedicarboxylic acid obtained in the first step with steam for the extraction of impurities.

2. The process according to claim 1, wherein the hydrogenation of the first step is performed under a hydrogen pressure between 2kg/cm<sup>2</sup> and less than 10kg/cm<sup>2</sup>.

3. The process according to claim 1 or 2, wherein the hydrogenation of the first step is performed in a pressure vessel provided with a vitreous layer.

4. The process according to claim 1, 2 or 3 wherein, in the second step, 1,4-cyclohexanedicarboxylic acid is brought continuously into contact in counterflow with steam by supplying the solution containing 1,4-cyclohexanedicarboxylic acid obtained in the first step continuously from one side of a packed tower, supplying steam continuously from the opposite direction thereof, withdrawing 1,4-cyclohexanedicarboxylic acid discontinuously or continuously from the other side while withdrawing steam in the opposite direction thereof and removing impurities extracted by the steam side by condensing them with the steam or by passing the steam through an alkaline aqueous solution before reheating for steam recycling as necessary.

## Patentansprüche

1. Verfahren zur Herstellung von 1,4-Cyclohexandicarbonsäure, gekennzeichnet durch die aufeinanderfolgende Durchführung der folgenden zwei Schritte:

- der erste Schritt umfaßt die Hydrierung einer Terephthalsäurehaltigen Lösung in Anwesenheit eines Palladiumkatalysators in einem hochsäurebeständigen Gefäß, das aus hochsäurebeständigen Metallen wie Hastelloy-Stahl, Inconel-Stahl und deren Kompakt bzw. Preßteil oder aus nichtmetallischen hochsäurebeständigen Materialien, wie Keramik, Email, Glas oder einem anderem glasartigen Material oder deren Kompakt bzw. Preßteil hergestellt ist, oder in einem Gefäß, das mit verschiedenen, säurebeständigen, hierin oben genannten Materialien ausgekleidet ist, und
- der zweite Schritt umfaßt das Inberührungbringen der Lösung, die die im ersten Schritt erhaltene 1,4-Cyclohexandicarbonsäure enthält, mit Dampf zur Extraktion von Verunreinigungen.

2. Verfahren nach Anspruch 1, wobei die Hydrierung des ersten Schritts unter einem Wasserstoffdruck von zwischen  $2 \text{ kg/cm}^2$  und weniger als  $10 \text{ kg/cm}^2$  durchgeführt wird.
3. Verfahren nach Anspruch 1 oder 2, wobei die Hydrierung des ersten Schritts in einem Druckgefäß durchgeführt wird, das mit einer glasartigen Schicht versehen ist.
4. Verfahren nach Anspruch 1, 2 oder 3, wobei im zweiten Schritt 1,4-Cyclohexandicarbonsäure kontinuierlich im Gegenstrom mit Dampf in Berührung gebracht wird, indem die Lösung, die die im ersten Schritt erhaltene 1,4-Cyclohexandicarbonsäure enthält, kontinuierlich von einer Seite eines Füll(körper)turms zugeführt wird, kontinuierlich von der gegenüberliegenden Richtung davon Dampf zugeführt wird, 1,4-Cyclohexandicarbonsäure diskontinuierlich oder kontinuierlich von der anderen Seite abgezogen wird, während Dampf in der gegenüberliegenden Richtung davon abgezogen wird und durch die Dampfseite extrahierte Verunreinigungen entfernt werden durch deren Kondensieren mit dem Dampf oder durch Hindurchleiten des Dampfes durch eine alkalische wäßrige Lösung vor einem Wiedererwärmen für Dampfrecycling, wie erforderlich.

## Revendications

1. Procédé de préparation de l'acide 1,4-cyclohexanedicarboxylique, caractérisé en ce que l'on passe successivement par les deux étapes suivantes :
  - la première étape comprend l'hydrogénation d'une solution contenant de l'acide téréphtalique, en présence d'un catalyseur au palladium, dans un récipient à résistance élevée aux acides, constitué de métaux à résistance élevée aux acides, tels que l'Hastelloy, l'Inconel et leurs agglomérés, ou de matériaux non métalliques à résistance élevée aux acides, tels que les céramiques, l'émail, le verre ou un autre matériau vitreux, et leurs agglomérés, ou dans un récipient revêtu intérieurement des divers matériaux résistant aux acides, mentionnés précédemment, et
  - la seconde étape comprend la mise en contact de la solution contenant de l'acide 1,4-cyclohexanedicarboxylique, obtenue dans la première étape, avec de la vapeur pour l'extraction des impuretés.
2. Procédé selon la revendication 1, dans lequel on réalise l'hydrogénation de la première étape sous une pression d'hydrogène supérieure ou égale à  $2 \text{ kg/cm}^2$  et inférieure à  $10 \text{ kg/cm}^2$ .
3. Procédé selon la revendication 1 ou 2, dans lequel on réalise l'hydrogénation de la première étape dans un récipient sous pression, muni d'un revêtement vitreux.
4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel, dans la seconde étape, on met l'acide 1,4-cyclohexanedicarboxylique en contact de manière continue, à contre-courant, avec de la vapeur en introduisant de manière continue la solution contenant l'acide 1,4-cyclohexanedicarboxylique, obtenue dans la première étape, par un côté d'une tour à remplissage, en introduisant de manière continue de la vapeur par le côté opposé, en extrayant de manière continue ou discontinue l'acide 1,4-cyclohexanedicarboxylique par l'autre côté tout en extrayant la vapeur dans la direction opposée, et en éliminant les impuretés extraites du côté vapeur en les condensant avec la vapeur ou en faisant passer la vapeur à travers une solution aqueuse alcaline avant chauffage pour recyclage de la vapeur si nécessaire.

*FIG. 1*

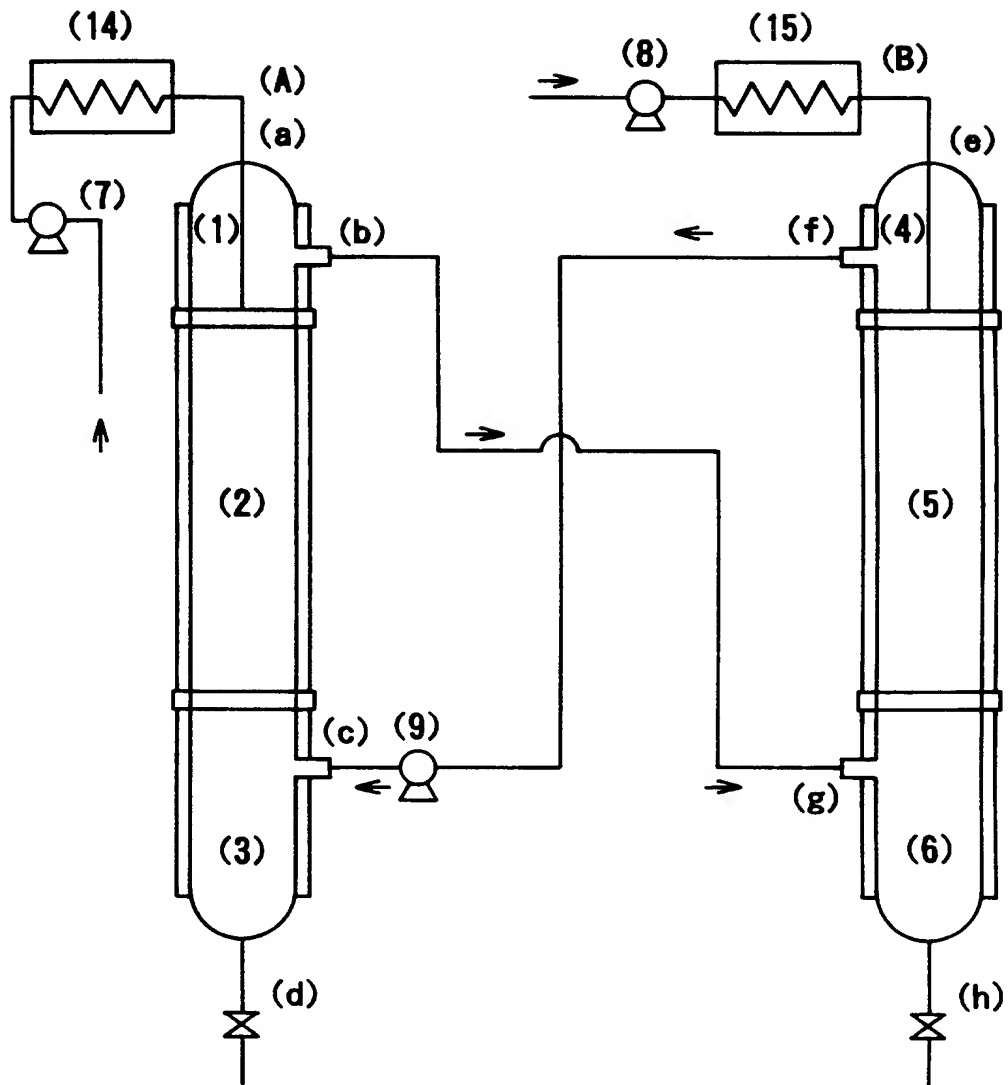


FIG. 2

